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silicon

Poly(diethylsiloxane) liquids. I. Action of sulfuric acid on diethyldiethoxysilane and its mixtures with triethylethoxysilane.

N. S. Leznov, L. A. Sabun and K. A. Andrianov. Zhur. Obshchei Khim. 29, 1270-5 (1959).

It was shown in work done in 1947 that H_2SO_4 reacts with $\text{Et}_2\text{Si}(\text{OEt})_2$ and its mixt. with Et_3SiOEt with the formation of poly(diethylsiloxanes) which are free of polymers contg. functional groups. Thus treatment of the polymer, formed by aq. hydrolysis of $\text{Et}_2\text{Si}(\text{OEt})_2$, with 96% H_2SO_4 1 hr. at 50° gave after aq. washing and neutralization a mixture of poly(diethylsiloxanes) with relatively greater mol. wt. through condensation of the linear polymers at the sites of originally residual EtO groups, as shown by high b.p. range of the polymers and essential absence of EtO groups. A similar effect is produced by contacting the polymers with HCO_2H (70°) or AcOH (90°). Addn. of concd. H_2SO_4 to $\text{Et}_2\text{Si}(\text{OEt})_2$ with cooling gave after stirring the mixt. at 20° to 100° a good yield of poly(diethylsiloxanes), whose mol. wt. and b.t. tended to rise with the rise of temp. of such treatment up to about 75° ; at higher temp. the formation of silanol sulfate esters and regeneration of H_2SO_4 become predominant and the tendency to form higher polymers declines sharply. In general, elevated temp. tends to favor the formation of ~~linear~~ polysiloxanes free of linear polymers contg. EtO groups. Heating $\text{Et}_2\text{Si}(\text{OEt})_2$ and Et_3SiOEt with H_2SO_4 2-3 hrs. at 75° gave ~~primarily~~ linear polymers with HO groups, formed by the aq. treatment of the initially formed sulfate esters. Increased amt. of Et_3SiOEt tends to block the formation of sulfate esters by blocking the HO end-groups of the polymers.

II. Action of phosphoric and boric acids on diethyldiethoxysilane and its mixtures with triethylethoxysilane. Ibid. 1276-81.

Heating $\text{Et}_2\text{Si}(\text{OEt})_2$ with 3:2 to 1:2 molar proportion of H_3BO_3 1-3 hrs. at 75° gave after an aq. treatment poly(diethylsiloxanes) contg. very little residual EtO groups, the products being 86-8% distillable cyclic polymers. Similar reaction with mixts. of $\text{Et}_2\text{Si}(\text{OEt})_2$ and Et_3SiOEt gave up to 92%

distillable poly-(diethylsiloxanes). Similar use of H_3BO_3 3-10 hrs. at 95° , finally at $130-140^\circ$ gave after an aq. treatment 35-54% distillable polysiloxanes with much linear polymer being formed. The reactions yielded as byproducts detectable amounts of $EtOPO_3H_2$ and $(EtO)_3B$. The distn. curves of distillable polysiloxanes formed with the use of H_3PO_4 or H_3BO_3 were quite similar.

Synthesis of polymers with inorganic molecular chains. I. Poly(organosiloxophosphorocaluminosiloxanes).

K. A. Andrianov, A. A. Zhdanov and A. A. Kazakova. Zhur. Obshchei Khim. 29, 1281-4 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 466.

Slow heating of 4.2 g. $(Et_3SiO)_3Al$ with 2.1 g. $Et_3SiOP(O)(OH)_2$ to 200-200° gave a distillate of $(Et_3Si)_2O$ and a residue of a polymer $Et_3SiO[Al(OSiEt_3)OP(O)(OSiEt_3)O]_{14}H$, sol. in MePh, EtOH and C_6H_6 . Similar reaction of a 2:1 molar ratio of the reactants 15 hrs. at 220° gave a distillate of H_2O and $(Et_3Si)_2O$ and a residue of viscous liquid polymer $[Et_3SiOAl(OSiEt_3)O]_2P(O)OSiEt_3$. Similarly 4.2 g. $(Et_3SiO)_3Al$ and 4.4 g. $(Et_3SiO)_3PO$ in 21.5 hrs. at 200-200° with a current of moist air drawn through the mixt., gave some H_2O and $(Et_3Si)_2O$, and a residue of transparent yellow resin, sol. in org. solvents and corresponding to $Et_3SiO[Al(OSiEt_3)OP(O)(OSiEt_3)O]_4SiEt_3$. The products pass into infusible insol. solids on being heated further. Similar reactions employing $Me_3SiOP(O)(OH)_2$ or $(Me_3SiO)_3PO$ proceeded very rapidly and directly gave insol. and infusible polymeric products. A kinetic study showed that the viscosity of the new polymers increases with the increasing amt. of distillate formed in the reaction. The starting materials were prep'd. as described previously (Voronkov, this j. 25, 469 (1955), and Andrianov et al. this j. 26, 267 (1956): $(Et_3SiO)_3PO$, b₅ 156-63°, n_D^{20} 1.4462; $(Me_3SiO)_3PO$, b₄ 77°, 1.4025; $Et_3SiOP(O)(OH)_2$; $Me_3SiOP(O)(OH)_2$, m. 66.5°.

Poly-(organometallosiloxanes). 2. Synthesis of poly-(organoaluminocobaltisiloxanes) and poly-(organoaluminonickelosiloxanes).

K. A. Andrienov and L. A. Khdanov (Inst. Hetero-org. Compds., Moscow).
Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1590-4. cf. Doklady
Akad. Nauk SSSR 114, 1005 (1957).

Polysiloxanes were synthesized which contain Al and Co or Ni atoms in the polymeric chain. Addn. of 12.99 g. CoCl_2 in 117 g. BuOH to 32.24 g. $\text{EtSi(OH)}_2\text{ONa}$ in 288 g. BuOH at 70° and heating 2.5 hrs. gave after filtration and evapn. a colorless resin which was free of Co. However, the reaction of 32.14 g. $\text{EtSi(OH)}_2\text{ONa}$, 3.67 g. AlCl_3 and 3.25 g. CoCl_2 in 400 g. BuOH at $80-100^\circ$ in 2 hrs. gave after filtration and evapn. 20.13 g. violet polymer, sol. in org. solvents and contg. 23% Si, 7.5% Al and 5.55% Co. Similarly $\text{PhSi(OH)}_2\text{ONa}$ gave a violet soluble polymer contg. 5.06% Al, 2.8% Co and 16% Si. Similar reaction of $\text{EtSi(OH)}_2\text{ONa}$ with AlCl_3 and NiCl_2 in BuOH gave a green polymer, sol. in org. solvents and contg. 6% Al and 1.9% Ni. A series of polymers was prepd. from $\text{EtSi(OH)}_2\text{ONa}$, AlCl_3 and CoCl_2 with different proportions of reactants. With increasing ratio of $\text{CoCl}_2/\text{AlCl}_3$ the polymers have progressively lower content of Al, but the content of Co shows a peak at about 1:1 molar ratio of original salts; this max. peak is about 10% Co in the polymer. The polymer prepd. from PhSi(OH)_3 (above) was fractionally pptd.; the richest fraction contained 14.28% Co, 4.4% Al and 15% Si. Removal of the solvent in vacuo from these products resulted in a loss of org. soly.

poly-(aluminophenylsiloxanes) - infusible but soluble polymers.

K. A. Anadrianov, A.A.Zhdanov and E.Z.Asnovich (Inst. Hetero-org. Compds. and All Union Electrotechn. Inst., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1760-6. Cf. Doklady Akad. Nauk USSR 102, 85 (1959). Addn. of PhSiCl_3 to H_2O at $20-5^\circ$ gave a layer of crude poly-(phenylsiloxane), which (25.8 g.) was treated with 8 g. 20% aq. NaOH and heated to $70-5^\circ$ while 16.63 g. 20% aq. $\text{Al}_2(\text{SO}_4)_3$ was being added in the presence of an unspecified org. solvent; the mixt. was stirred 2 hrs. at 75° and the sepd. and washed org. layer was evapd. leaving a residue of polymeric product corresponding to repeating units of $\text{C}_{24}\text{H}_{22}\text{Si}_4\text{AlO}_{8.5}$. A similar product was obtained by addn. of 40 g. PhSiCl_3 to 28.7 g. 20% NaOH and 12.5 g. 10% aq. $\text{Al}_2(\text{SO}_4)_3$ in the presence of an org. solvent. The product evidently contains 4 Si units per 1 Al unit, with approximately 2 HO groups (on Si atoms) per repeating unit. Fractional pptn. of the product from CCl_4 with petr. ether gave fractions ranging in mol. wt. from 5990 to 11800. A similar material was prepd. from EtSiCl_3 and corresponded to repeating units $\text{C}_{10}\text{H}_{27}\text{Si}_5\text{AlO}_{10}$. The Ph deriv. was sol. in MePh, EtOH, Me_2CO and PhCl. On being heated to $200-500^\circ\text{C}$, the product became less and less sol. in org. solvents. However the polymer does not melt even at 500°C . Evidently heating converts it to a tridimensional product with extensive crosslinking. The Et deriv. could not be pressed into a mold at 210° as it remained a friable powder. This polymer preserved its org. soly. after being heated to 200° for several hrs. but the soly. is lost rapidly after that period especially at still higher temps. The polymers, prior to being heated, are sol. in many common org. solvents and evidently are constituted on the basis of a complex cyclic structure.

Synthesis of organosilicon compounds containing the methacrylyl group.

K.A. Andrianov and A.K. Dabagova (Inst. Hetero-org. Compds., Moscow).

Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1767-71.

cf. this j. 1957, 459.

Heating in a rotating autoclave a mixt. of 38.1 g. $\text{ClCH}_2\text{SiMe}_2\text{OEt}$ (45.5 g. $\text{ClCH}_2\text{SiMe}(\text{OEt})_2$, 45 g. $\text{ClCH}_2\text{SiMe}_2\text{OBu}$, 59.6 g. $\text{ClCH}_2\text{SiMe}(\text{OBu})_2$ or 74.1 g. $\text{ClCH}_2\text{Si}(\text{OBu})_3$) with 37.2 g. $\text{CH}_2:\text{CMeCO}_2\text{K}$, 5 g. powd. Cu and 0.3 g. hydroquinone 3.5 hrs. at 180° gave the following products: $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}_2\text{OEt}$ (I), b_5 $72\frac{2}{3}^\circ$, d_{20} 0.9421, n_D^{20} 1.4300; $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}(\text{OEt})_2$, b_5 $97\text{--}100^\circ$, 0.9753, 1.4260; $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}_2\text{OBu}$, b_5 $86\text{--}7^\circ$, 0.9263, 1.4320; $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}(\text{OBu})_2$, b_5 $126\text{--}7^\circ$, 0.9458, 1.4345; $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{Si}(\text{OBu})_3$, b_5 $144\text{--}45^\circ$, 0.9610, 1.4370. The reaction may be also run at atm. pressure at reflux for 2 hrs., the yields being about 30%. To 12.1 g. I and 4.4 g. $(\text{AcOSiMe}_2)_2\text{O}$ there was added with cooling 5% by wt. of EtOSO_3H contg. 2% H_2O and the mixt. was kept 2 days; the sepd. org. layer was neutralized with NaHCO_3 and distd. yielding 25-33% $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}_2(\text{OSiMe}_2)_2\text{CH}_2\text{O}_2\text{CMe}$ (CH_2 , b_2 $147\text{--}8^\circ$, 0.9862, 1.4390. Similarly were prepd.: $\text{Me}_3\text{SiOSiMe}(\text{OSiMe}_3)\text{CH}_2\text{O}_2\text{CCMe}:\text{CH}_2$, b_2 $90\text{--}1^\circ$, 0.9170, 1.4150; $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}_2(\text{OSiMe}_2)_2\text{CH}_2\text{O}_2\text{CCMe}:\text{CH}_2$, b_2 $162\text{--}3^\circ$, 0.9953, 1.4360; and $\text{CH}_2:\text{CMeCO}_2\text{CH}_2\text{SiMe}_2(\text{OSiMe}_2)_2\text{CH}_2\text{O}_2\text{CCMe}:\text{CH}_2$, b_2 $177\text{--}8^\circ$, 0.9941, 1.4330. Refluxing 101.5 g. 1,2-dichlorotetramethyldisiloxane or 138.5 g. 1,3-dichlorohexamethyltrisiloxane with 112 g. Ac_2O gave a distillate of AcCl and resp. 1,2-diacetoxytetramethyldisiloxane, b_{22} $94\text{--}8^\circ$, and 1,3-diacetoxyhexamethyltrisiloxane, b_{50} $140\text{--}2^\circ$ in 60-75% yields. These were: $\text{AcOSiMe}_2\text{OSiMe}_2\text{OAc}$, $b.$ 189° , 1.0232, 1.4010 and $\text{AcOSiMe}_2(\text{OSiMe}_2)_2\text{OAc}$, $b.$ 212° , 1.0131, 1.4030.

Chloromethylation reaction of arylaliphaticdisiloxanes. Synthesis of chloromethylbenzyltrimethylchlorosilane and its derivatives.

K. A. Andrianov, A. A. Zhdanov and V. A. Odinetz. Doklady Akad. Nauk S.S. S. R. 130, 75-8 (1960).

cf. Zhur. Obshchei Khim. 29, 1499 (1959).

Stirring 55.5 g. $\text{PhCH}_2\text{SiMe}_2\text{Cl}$ with 10 g. paraformaldehyde and 100 ml. concd. HCl 4-5 hrs. at 60° while dry HCl was being passed into the mixt. gave an upper layer contg. the chloromethylated material. This crude

substance treated with ice and Et_2O gave 60 g. liquid product contg.

(I) $(\text{ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_2)_2\text{O}$. This (60 g.) and 24 g. NH_4Cl was treated with

60 g. concd. H_2SO_4 with ice cooling 15-20 min. and the liq. layer gave

on distn. 26 g. $\text{ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{Cl}$, b_5 133° , d_{20} 1.1139, n_D^{20} 1.5234.

This with H_2O gave pure I, b_5 232° , 1.0917, 1.5275. When the chloromethylation was attempted in the presence of ZnCl_2 , the reaction mixt. gave

only a viscous undistillable polysiloxane, evidently $(\text{OSiMe}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_2)_n$. I heated 10 hrs. at 120° with KOAc-AcOH gave $(\text{AcOCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_2)_2\text{O}$, b_5 $268-70^\circ$, 1.0622, 1.5130, which hydrolyzed with EtOH-KOH

in 1 hr. to a product which showed signs of partial reaction or decompn. during attempted distn., leaving a residue of apparently $\text{Me}_2\text{Si}(\text{OSiMe}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH})_2$.

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Vinylloxysilanes.

A. N. Nesmeyanov, I. F. Lutsenko and V. A. Bratshev (M.V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 128, 551-4 (1959).

To 32 g. $\text{Hg}(\text{CH}_2\text{CH})_2$ in 70 ml. isopentane there was added 11 g. Me_3SiCl in 20 ml. isopentane and after refluxing 2 hrs. the filtered mixt. gave 72% $\text{Me}_3\text{SiOCH:CH}_2$, b. $74-5^\circ$, n_D^{20} 1.3835, d_{20} 0.7720. Similarly were prepd. 89% $\text{Et}_3\text{SiOCH:CH}_2$, b_{20} $53-4^\circ$, 1.4275, 0.8505; 77% $\text{ClCH}_2\text{SiMe}_2\text{OCH:CH}_2$, b_{42} $54-5^\circ$, 1.4329, 0.9796; 86% $(\text{ClCH}_2)_2\text{SiMeOCH:CH}_2$, b_{14} $73-3.5^\circ$, 1.4646, 1.1515; 64% $\text{Me}_2\text{Si}(\text{OCH:CH}_2)_2$, b. $108.5-9^\circ$, 1.4052, 0.8792; 79% $\text{Et}_2\text{Si}(\text{OCH:CH}_2)_2$, b_{40} $69-70^\circ$, 1.4246, 0.8890; 82% $\text{MePhSi}(\text{OCH:CH}_2)_2$, $b_{1.5}$ $65-6^\circ$, 1.4940, 0.9959; ~~61%~~ 81% $\text{ClCH}_2\text{SiMe}(\text{OCH:CH}_2)_2$, b_{36} $72.5-3^\circ$, 1.4386, 1.0457; 71% $\text{MeSi}(\text{OCH:CH}_2)_3$, b_{30} $50-1^\circ$, 1.4133, 0.9457; 76% $\text{EtSi}(\text{OCH:CH}_2)_3$, b_{40} $69-70^\circ$, 1.4225, 0.9503; 70% $\text{PhSi}(\text{OCH:CH}_2)_3$, b_2 $79-60^\circ$, 1.4896, 1.0385; 72% $\text{Si}(\text{OCH:CH}_2)_4$, b_{12} $52-3^\circ$, 1.4146, 0.9949. To 125 g. ClHgCH_2Ac in C_6H_6 there was added 32 g. pyridine and 17 g. SiCl_4 in C_6H_6 ; after 1.5 hrs. refluxing the filtered mixt. gave 49% $\text{Si}(\text{OCMe:CH}_2)_4$, b_5 76° , 1.4320, 0.9722. Similarly were obtained: 58% $\text{Et}_3\text{SiOCMe:CH}_2$, b_{20} $65-6^\circ$, 1.4290, 1.8365(???); 63% $\text{Et}_3\text{SiOCEt:CHMe}$, b_3 $55-6^\circ$, 1.4432, 0.8497; 45% $\text{Et}_3\text{SiOCPH:CH}_2$, b_3 $106-7^\circ$, 1.5089, 0.9466; 87% $(\text{EtO})_3\text{SiOCH:CH}_2$, b_{30} $76-7^\circ$, 1.3905, 0.9493.

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Reactivity of α -, β - and γ -chloroalkylsilane chlorides in the Friedel-Crafts reaction.

B. A. Chernyshev and M. E. Dolgaya (Inst. Org. Chem., Acad. Sci., Moscow).

Zhur. Obshchei Khim. 29, 1850-3 (1959). cf. 28, 2829(1958).

Detn. of the rates of HCl evolution in a Friedel-Crafts reaction of various chloroalkylsilane chlorides and C_6H_6 gave the following reaction rate constants at 30° : Cl_3SiCH_2Cl 2.36×10^{-4} mole/min.; $Cl_3SiCH_2CH_2Cl$ 4.28×10^{-3} ; $Cl_3Si(CH_2)_3Cl$ 5.48×10^{-3} ; $MeSiCl_2CH_2Cl$ 3.67×10^{-4} ; $MeSiCl_2(CH_2)_2Cl$ 4.47×10^{-2} ; $EtSiCl_2(CH_2)_2Cl$ 4.17×10^{-2} ; $MeSiCl_2(CH_2)_3Cl$ 6.72×10^{-3} ; $Cl_3SiCHMeCl$ 2.39×10^{-4} ; $EtSiCl_2CHMeCl$ 2.96×10^{-4} . Reaction of $Cl_3Si(CH_2)_2Cl$ with $PhCl$ had the rate constant of 1.67×10^{-3} and with $MePh$ 5.95×10^{-3} .

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Synthesis and transformations of unsaturated organosilicon compounds.

II. Synthesis of silicohydrocarbons of vinylacetylene series.

I. A. Shikhiev, M. F. Shostakovskii and L. A. Kayutenko (Inst. Org.Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 2137-9 (1959). cf. Doklady Akad. Nauk SSSR 109, 344(1956).

Heating 15 g. bis-(1,1-dimethyl-2-propyne-1-ol)-ethylsilane with 13.6 g. TiSO_4 in the presence of hydroquinone to 65° gave after distn. an unstated yield of $(\text{CH}_2:\text{CMeC}\equiv\text{C})_2\text{SiH}_2\text{Et}$, b_4 $76-7^\circ$, n_D^{20} 1.5010, d_{20} 0.8518. Similarly were prepd.: $(\text{CH}_2:\text{CMeC}\equiv\text{C})_2\text{SiMe}_2$, b_4 $75-5.5^\circ$, 1.5000, 0.8475; $(\text{CH}_2:\text{CMeC}\equiv\text{C})_2\text{SiEt}_2$, b_6 105° , 1.5027, 0.8594; $(\text{CH}_2:\text{CMeC}\equiv\text{C})_2\text{SiMeEt}$, b_2 $87-8^\circ$, 1.5000, 0.8583; $(\text{CH}_2:\text{CMeC}\equiv\text{C})_2\text{SiEtPr}$, b_{10} 113° , 1.4990, 0.8555. These hydrogenated to the satd. analogs over Raney Ni in MeOH.

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Organomagnesium synthesis of α - and β -trimethylsilylacrylic acids and vinyl derivatives of silicon, germanium and tin.

V. F. Mironov, A. D. Petrov and M. G. Maksimova (N.D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1954-60.

The Normant method was used to prepare the following substances. RMgX from 11 g. Mg and 50 g. $\text{CH}_2\text{:CHBr}$, activated by a little PBr_3 , in tetrahydrofuran, was treated with Et_3SnCl , yielding 60% $\text{Et}_3\text{SnCH:CH}_2$, b. $174-5^\circ$, n_D^{20} 1.4780, d_{20} 1.2133. Similarly was prepd. 55% $\text{Et}_2\text{Ge}(\text{CH:CH}_2)_2$, b₇₄₅ 149.8° , 1.4575, 1.0193; 22% $\text{EtSiH}(\text{CH:CH}_2)_2$, b. $93-4.6^\circ$, 1.4305, 0.7554; $\text{Et}_2\text{Si}(\text{CH:CH}_2)_2$, b₇₄₆ 133.3° , 1.4435, 0.7911; $\text{MePhSi}(\text{CH:CH}_2)_2$, b₁₁ $93.5-4.5^\circ$, 1.5185, 0.9069; $\text{MeEtSi}(\text{CH:CH}_2)_2$, b₇₄₅ 111° , 1.4295, 0.7623; $\text{MeSi}(\text{CH:CH}_2)_3$, b₇₄₇ 101.9° , 1.4405, 0.7692; $\text{EtSi}(\text{CH:CH}_2)_3$, b_{744.5} 133.6° , 1.4525, 0.7930; $\text{Et}_2\text{Sn}(\text{CH:CH}_2)_2$, b₇₆₅ 168.5° , 1.4850, 1.2356. Addn. of Br_2 to $\text{MeSiCl}_2\text{CH:CH}_2$ under incandescent lamp with cooling gave 94% $\text{MeSiCl}_2\text{CHBrCH}_2\text{Br}$, b₄ 101° , 1.5335, 1.9221. Similarly was prepd. 90% $\text{EtSiCl}_2\text{CHBrCH}_2\text{Br}$, b₇₃₉ 240° , b₇ 142° , 1.5320, 1.8227. Distn. of $\text{BrCH}_2\text{CHBrSiCl}_3$ from quinoline or PhNEt_2 gave 65% $\text{CH}_2\text{:CHBrSiCl}_3$, b₇₄₉ 145.5° , 1.4928, 1.7151. Similarly was prepd. 55% $\text{CH}_2\text{:CHBrSiMeCl}_2$, b₇₃₅ $143-3.5^\circ$, 1.4870, 1.5594, and $\text{CH}_2\text{:CHBrSiEtCl}_2$, 40%, b₂₀ 135° , 1.4370, 1.4458. MeMgI and $\text{CH}_2\text{:CHBrSiCl}_2$ gave 74% $\text{CH}_2\text{:CHBrSiMe}_3$, b₄₁ $47-8^\circ$, b₇₄₅ 124° , 1.4580, 1.1562 (Raman spectrum shown). EtMgBr similarly gave 30% $\text{Et}_3\text{SiCHBr:CH}_2$, b₃₅ 92° , 1.4770, 1.1273. Heating 578 g. $\text{BrCH}_2\text{CH}_2\text{SiCl}_3$ with 1 g. AlCl_3 gave 23.7% BrCH:CHSiCl_3 , b. $155-6^\circ$, 1.5030, 1.7207. This with MeMgCl gave 42% BrCH:CHSiMe_3 , b₄₂ 55° , 1.4675, 1.1628 (Raman spectrum shown). This with Mg in tetrahydrofuran gave the RMgBr which with Me_3SiCl gave only $\text{Me}_3\text{SiCH:CHSiMe}_3$. Carbonation of the above RMgBr gave 64% $\text{Me}_3\text{SiC}(\text{:CH}_2)\text{CO}_2\text{H}$, b₁₃ $97-105^\circ$, m. 50° . Similarly was prepd. 46% $\text{Me}_3\text{SiCH:CHCO}_2\text{H}$, b₁₃ 113° , n_D^{25} 1.4500, m. $25-5.5^\circ$.

silicon

Reaction of tetraalkyldihydrosiloxanes with difunctional unsaturated compounds.

V. V. Korshak, A. M. Polyakova, V. M. Vdovin, V. F. Mironov and A. P. Petrov (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 128, 960-3 (1959). cf. Izvest. Akad. Nauk SSSR, otd.kh.nauk, 1929, No.12, no pp given. It was shown that dihydrosiloxanes add to organometallic compds. with 2 unsatd. radicals and yield polymeric products. Unsatd. Si and Ge compds. react satisfactorily, while those of Sn do not react and those of Pb undergo a decompn. with loss of Pb. Treatment of MeSiHCl_2 with EtMgCl gave 67% MeEtSiHCl , b. $85-96^\circ$, which treated with $\text{H}_2\text{O}-\text{Et}_2\text{O}$ gave 88.5% $\text{O}(\text{SiHMeEt})_2$, b. $125.5-6^\circ$, n_D^{20} 1.3980, d_{20} 0.7935. Similarly was prepd. 88% ~~$\text{O}(\text{SiHMeEt})_2$~~ Et_2SiHCl , b. $98.5-101.5^\circ$, n_D^{20} 1.4154, which gave 75-93% $\text{O}(\text{SiHEt}_2)_2$, b. $172-3^\circ$, 1.4160 , 0.8159 . EtMgBr and EtSiHCl_2 gave Et_2SiH and $\text{O}(\text{SiHEt}_2)_2$ after an aq. treatment. Similarly was prepd. $\text{O}(\text{SiMe}_2\text{H})_2$, b. $70-1^\circ$, 1.3700 , 0.7572 . The dihydrosilanes above were shaken in sealed ampuls with: $\text{Et}_2\text{Si}(\text{CH}:\text{CH}_2)_2$, $\text{PhMeSi}(\text{CH}:\text{CH}_2)_2$, $\text{Et}_2\text{Ge}(\text{CH}:\text{CH}_2)_2$, $\text{Me}_2\text{Ge}(\text{CH}_2\text{CH}:\text{CH}_2)_2$, $\text{Et}_2\text{Si}(\text{CH}_2\text{CH}:\text{CH}_2)_2$, $\text{Me}_2\text{Si}(\text{OCH}_2\text{CH}:\text{CH}_2)_2$, $\text{Et}_2\text{Si}(\text{OCH}_2\text{CH}:\text{CH}_2)_2$ or $\text{Me}_2\text{Si}(\text{CH}_2\text{CH}:\text{CH}_2)_2$, in the presence of 0.01 g. per 0.12 mole of H_2PtCl_6 catalyst; the reactions were then completed by 6 hrs. at 120° . All the listed monomer combinations yielded appropriate polymeric products, the analyses of which are reported.

silicon

Synthesis of α,ω -bis-(cyanoalkyl)-tetra-alkyldisiloxanes.

A. D. Petrov, V. M. Vdovin and R. Sultanov (N.D. Zelinskii Inst. Org. Chem., Moscow), Doklady Akad. Nauk S.S.S.R. 128, 1204-7 (1959). cf. this j. 100, 711 (1955).

Stirring 19.3 g. $\text{NC}(\text{CH}_2)_3\text{SiMeEtCl}$ with 25 ml. H_2O 5 hrs. gave after extn. with Et_2O 10.3 g. $(\text{NC}(\text{CH}_2)_3\text{SiMeEt})_2\text{O}$, b_3 195-7°, b_3 193° (redistd.), n_D^{20} 1.4513, d_{20} 0.9377. This was also formed from $\text{NC}(\text{CH}_2)_3\text{SiEtCl}_2$ and MeMgCl , followed by treatment with H_2O . Similarly were prepd.: $\text{NC}(\text{CH}_2)_3\text{SiEtCl}_2$, b_3 99°, 1.4625, 1.1295; $\text{NC}(\text{CH}_2)_3\text{SiMeEtCl}$, b_4 121°, 1.4515, 0.9895; $\text{NC}(\text{CH}_2)_3\text{SiEtMe}_2$, b_3 66°, 1.4363, 0.8377; $\text{NC}(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\text{SiMeEtCl}$, b_1 123°, 1.4555, 1.0098; $(\text{NCCH}_2\text{CH}_2\text{SiEt}_2)_2\text{O}$, b_2 175°, 1.4605, 0.9470; $(\text{NCCH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)_2\text{O}$, b_2 161-2°, 1.4441, 0.9344; $(\text{NCCH}_2\text{CH}_2\text{CH}_2\text{SiEt}_2)_2\text{O}$, $b_{1.5}$ 193°, 1.4593, 0.9413; $(\text{NCCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiMeEt})_2\text{O}$, undistillable, 1.4552, 0.9741. Stirring I with concd. HCl finally at 80-90° gave $(\text{HO}_2\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SiMeEt})_2\text{O}$, an oil. To 160 g. NCCH_2CH_2 , 90 g. PhNEt_2 mixt. there was added over 8 hrs. 410 g. HSiCl_3 at reflux, and after 32 hrs. further refluxing there was obtained some $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CN}$, b_{15} 96-8°, m. 26-30°, sepd. from PhNEt_2 by freezing-out.

Addition of hydrosilanes to dimethylvinylethynylcarbinol and the product of its cyanoethylation.

A. D. Petrov and S. I. Sadykh-Zade (N.D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 129, 58⁴₈-7 (1959). cf. this j. 112,662(1957).

Addn. of 53 g. Et_3SiH to 55 g. $\text{CH}_2:\text{CHC}:\text{CCMe}_2\text{OH}$ and 0.5 ml. 0.1 N H_2PtCl_6 (I) and heating the mixt. to 170° gave 62% $\text{CH}_2:\text{CHC}(\text{SiEt}_3):\text{CHCMe}_2\text{OH}$, b_1 $85-5.5^\circ$, n_D^{20} 1.4861, d_{20} 0.8873. Similarly $\text{NCCH}_2\text{CH}_2\text{OCMe}_2\text{C}:\text{CCH}:\text{CH}_2$ and EtSiHCl_2 reacted in iso-PrOH in the presence of H_2PtCl_6 at 90° (very exothermic) and gave 61% $\text{NCCH}_2\text{CH}_2\text{OCMe}_2\text{CH}:\text{C}(\text{SiEtCl}_2)\text{CH}:\text{CH}_2$, b_3 $150-1^\circ$, 1.4865, 1.0846. Similarly was prepd. $\text{CH}_2:\text{CHC}(\text{SiEt}_3):\text{CHCMe}_2\text{OCH}_2\text{CH}_2\text{CN}$, 75%, b_3 158° , 1.4840, 0.9196; 54% $\text{CH}_2:\text{CHC}(\text{SiMeCl}_2):\text{CHCMe}_2\text{OCH}_2\text{CH}_2\text{CN}$, b_4 $146-8^\circ$; 90% 2-methyl-4-(triethylsilyl)-1,3,5-hexatriene, b_3 91° , 1.4920, 0.8759, was obtained by treating I with KHSO_4 .

Silicon

Addition of trichlorosilane to dialkyl(phenyl, chloro)-diallylsilanes in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$.

A. V. Topchiev, N. S. Nametkin and S. G. Durgar'yan. Doklady Akad. Nauk S.S.S.R. 130, 105-8 (1960). cf. Sommer et al. JACS 69, 188 (1947).

The following silanes were prepd. by addn. of HSiCl_3 to various diallylsilanes in the presence of 1 ml. catalyst composed of M soln. of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in iso-PrOH with heating 10 hrs. at 50° and 2 hrs. at 80° : 28.5% $\text{CH}_2:\text{CHCH}_2\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3$, b_7 115- 8° ; 29% $\text{CH}_2:\text{CHCH}_2\text{SiEt}_2(\text{CH}_2)_3\text{SiCl}_3$, b_4 124- 6° ; 29.7% $\text{CH}_2:\text{CHCH}_2\text{SiPr}_2(\text{CH}_2)_3\text{SiCl}_3$, b_9 167- 9° ; 28.8% $\text{CH}_2:\text{CHCH}_2\text{SiBu}_2(\text{CH}_2)_3\text{SiCl}_3$, b_9 186- 9° ; 17.6% $\text{CH}_2:\text{CHCH}_2\text{SiPh}_2(\text{CH}_2)_3\text{SiCl}_3$, b_4 222- 4° ; 13.8% $\text{CH}_2:\text{CHCH}_2\text{SiMePh}(\text{CH}_2)_3\text{SiCl}_3$, b_5 180- 2° ; 8.3% $\text{CH}_2:\text{CHCH}_2\text{SiCl}_2(\text{CH}_2)_3\text{SiCl}_3$, b_4 153- 6° ; $\text{Me}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3)_2$, 27.9%, b_{55} 163- 5° ; 32% $\text{Et}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3)_2$, b_5 176- 8° ; 32.6% di-Pr analog, b_5 193- 5° ; 34% di-Bu analog, b_5 219- 21° ; 52.4% di-Ph analog, b_4 268- 70° ; 41.4% $\text{MePhSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3)_2$, b_5 212- 4° ; 67.3% $\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_3)_2$, b_2 210- 2° .

*silicon***Synthesis of organosilicon monomers from methylchlorosilane.**

V. A. Ponomarenko, G. V. Odabashyan and A. D. Petrov (N.D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 130, 333-5 (1960). cf. 126, 1009 (1959).

Slow distn. through a column of 200 g. MeSiHCl_2 and 14 g. activated dimethylcyanamide gave MeSiH_2Cl , $b_{745} 8-9^\circ$, ~~xxx~~ which was added to appropriate unsatd. compds/ conventionally in the presence of H_2PtCl_6 . EtSiH_2Cl was employed similarly. The following products are listed: MeEtSiHCl , MeEt_2SiCl , MePrSiHCl , $\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiHCl}$, $\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiCl}$, $\text{MeEtSiClCH}_2\text{CH}_2\text{CF}_3$, $\text{MeEtSiClCH}_2\text{CH}_2\text{SiClMeEt}$ and $\text{MePhSiClCH}_2\text{CH}_2\text{SiClMePh}$. The yields were 18-69%.

Passage of MeSiHCl and PhCl through a hot tube at $635-45^\circ$ gave a range of products from which was isolated 15.5% MePhSiHCl , $b_{740} 176^\circ$, $d_{20} 1.0540$, $n_D^{20} 1.5171$. This was similarly added to various unsatd. compds. Passage of MeSiH_2Cl and $\text{CH}_2:\text{CHCl}$ through a tube at $550-600^\circ$ gave 11.5% $\text{Me}(\text{CH}_2:\text{CH})\text{SiHCl}$, $b_{761} 60.5^\circ$, 0.9125, 1.4140. Also listed are: MePhSiHCl , $b_{740} 176^\circ$, 1.0540, 1.5171; MePhSiCl_2 , $b_{740} 197^\circ$, 1.1814, 1.5194; $\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiHCl}$, $b_{746} 96.5^\circ$, 1.1565, 1.3651; $\text{Me}(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiCl}$, $b_6 45.5-7^\circ$, 1.2791, 1.3699; ~~MePh~~ $\text{MeEtSi}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{Cl}$, $b_{758} 140^\circ$, 1.1044, 1.3871; $\text{MeEtSiClCH}_2\text{CH}_2\text{SiClMeEt}$, $b_{10} 100.5-1.5^\circ$, 0.9981, 1.4580; $\text{MePhClSiCH}_2\text{CH}_2\text{SiClMePh}$, $b_9 207-9^\circ$, m. $59-60^\circ$.

Reaction of tetra-alkyldihydrodisiloxanes with difunctional unsaturated compounds.

L. M. Polvakova and N. A. Chumakovskii. Doklady Akad. Nauk S.S. S.R. 130, 1037-40 (1960).

Infra-red spectra are shown for the reaction products of $(R_2SiH)_2O$ with unsatd. difunctional compds. centered on Si or Ge atoms and contg. 2 vinyl groups (cf. this j. 128, 930(1959) for the prepn.). Spectra are also shown for the following monomers: $(Me_2SiH)_2O$, $(MeEtSiH)_2O$, $(Et_2SiH)_2O$, $MePhSi(CH:CH_2)_2$, $Et_2Si(CH:CH_2)_2$, $Et_2Si(CH:CH_2)_2$ and $CH_2:CHCH_2CH_2CH:CH_2$. The polymeric products from ~~xxx~~ the selected monomer pairs fail to show any residual Si-H frequencies in their spectra, after reppn. from EtOH.

The Si-H bond frequency does appear in spectra of products formed from excess disiloxane component reacting with the divinyl deriv. as it does in the polymer formed from the reaction with 2,5-hexadiene. Diallylic derivs. tend to produce products with residual vinyl or C:C bonding. It is suggested that the divinyl monomers reacting with equimolar amounts of the disiloxanes yield products which are probably cyclic in nature, while the diallylic monomers tend to yield linear products.

silicon

Organic compounds of boron.

B. M. Mikhailov. Uspekhi Khim. 28, 1450-87 (1959).

A review, covering the synthesis and the general properties of organo-boron compds, with 176 references through 1958.

Organoboron

Organoboron compounds. XXXIV. Alkylphenylboron chlorides.

B. M. Mikhailov and P. M. Aronovich (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 1254-7 (1959); cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 546.

Treatment of 127 ml. (iso-BuO)₂BPh in Et₂O at -70° over 3-4 hrs. with MeMgBr from 13.4 g. Mg, stirring 4-5 hrs. and setting the mixt. aside at -70° overnight gave after treatment with aq. HCl 71% iso-BuOBMePh, b₇ 88-9°, n_D²⁰ 1.4362, d₂₀ 0.8940. Similar reaction with EtLi gave 68.5% iso-BuO-BEtPh, b₈ 95-6°, 1.4828, 0.8923, which on prolonged heating to 100° undergoes disproportionation. Shaking iso-BuOERPh with 36% HCl resulted in a homogeneous soln. in 1-2 days which yielded ROH on distn. along with some unreacted ester. Treatment of 0.2 mole iso-BuOERPh with 37.5 g. PCl₅ at 60-70° 10-15 min. gave: 81% PhMeBCl, b₂₄ 68-9°, d₂₀ 1.0440; 83.3% PhEtBCl, b₂₀ 85-6°, 1.0328; 76.4% PhPrBCl, b₉ 83-4°, 1.0274; 82.5% PhBuBCl, b₇ 90-1°, 0.9966.

Organoboron compounds. XXXV. Alkylphenylboronic acids and their anhydrides. B. M. Mikhailov and P. M. Aronovich (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 1257-62 (1959). cf. 29, 1254 (1959).

Addn. of 0.1 mole PhRBCl in 1 vol. Et_2O to 16.5 ml. 20% NaOH with ice cooling, shaking and extn. of the aq. layer with Et_2O , gave after washing the combined org. layers with H_2O , drying and evapg. in vacuo the following liquid and very easily oxidizable PhRBCH : (R shown) Me, 85%, n_D^{20} 1.5202, d_{20} 0.9729; Et, 78.5%, 1.5102 (at 24°), 0.9514 (at 24°); Pr, 82.4%, 1.5030, 0.9429; Bu, 90%, 1.4987, 0.950. Distn. of these in vacuo gave $(\text{PhRB})_2\text{O}$: Me, b_8 $137-8^\circ$, 1.5440, 0.9666; Et, b_3 $130-2^\circ$, 1.5419 (at 24°), 0.9526 (at 24°); Pr, b_5 $156-8^\circ$, 1.5343, 0.9575; the Bu member gave a range of products with $b_{0.3}$ $110-65^\circ$ and left a residue of phenylboronic anhydride. Shaking 1 g. $(\text{PhEtB})_2\text{O}$ with 3 ml. Et_2O and 1 ml. H_2O 1 hr. gave on evapn. of the org. layer a liquid residue of PhEtDOH , n_D^{24} 1.5130. If the hydrolysis is run with 20% NaOH , the aq. layer yields 96% $\text{PhEtB(OH)}_2\text{Na}$, needles (from Me_2CO) which are very hygroscopic. Similarly was prepd. 89% $\text{PhPrB(OH)}_2\text{Na}$, needles.

MePhBCl and $\text{H}_2\text{O}-\text{Et}_2\text{O}$ mixed with ice cooling gave after evapn. a mixture of methylboronic and methylphenylboronic acids. PhEtBCl similarly gave mainly ethylboronic acid, while PhPrBCl gave mixed propylphenylboronic and propylboronic acids. PhBuBCl gave some butylboronic acid. Keeping PhEtDOH in concd. $\text{HCl}-\text{Et}_2\text{O}$ (exothermic reaction on mixing) gave after 1 day some C_6H_6 and ethylboronic acid; the same ester kept in $\text{Et}_2\text{O}-\text{HCl}$ 3 days showed no change. Evidently hydrolysis of PhRBCl is accomplished through initial complex formation of H_2O at the B atom, followed by loss of C_6H_6 .

Organoboron compounds. XXXVI. Synthesis of hexa-substituted borazole from esters of arylchloroboronic acids.

B. M. Mikhailov and T. V. Kostroma (Inst. Org. Chem., Acad. Sci., Moscow) Zhur. Obshchei Khim. 9, 1477-83 (1959). cf. Izvest. Akad. Nauk SSSR 1957, 1125.

Heating esters of aryloethylaminoboronic acids to 300° converts them to borazoles and esters of arylboronic acids. To 14.3 g. $o\text{-MeC}_6\text{H}_4\text{BClOCH}_2\text{CHMe}_2$ in 20 ml. Et_2O there was added at -30° 8.75 ml. EtNH_2 in Et_2O and after 0.5 hr. at -30° and 1 hr. at room temp., the mixt. was filtered and rapidly distd. yielding 84% $o\text{-MeC}_6\text{H}_4\text{B}(\text{OCH}_2\text{CHMe}_2)_2\text{NHEt}$, b_3 $93-5^{\circ}$, n_D^{20} 1.4847, d_{20} 0.9042. This heated to 260° does not form a borazole, being different in this respect from the other esters below. Similarly was prepd. 59.4% $p\text{-MeC}_6\text{H}_4\text{B}(\text{OCH}_2\text{CHMe}_2)_2\text{NHEt}$, b_2 $110-12^{\circ}$, 1.4891, 0.9059; 52.4% $1\text{-C}_{10}\text{H}_7\text{B}(\text{OCH}_2\text{CHMe}_2)_2\text{NHEt}$, b_9 $188-5^{\circ}$, 1.5470, 0.9750. I (9.8 g.) heated 1 hr. at 260° , cooled and extd. with isopentane gave a ppt. of 1.2 g. B,B,B-tri-*p*-tolyl-N,N,N-triethylborazole, m. $222-5^{\circ}$. The filtrate gave 5.64 g. mixed ~~pr~~ starting ester and $p\text{-MeC}_6\text{H}_4\text{B}(\text{OCH}_2\text{CHMe}_2)_2$. To 19.65 g. $\text{PhBClOCH}_2\text{CHMe}_2$ in 20 ml. Et_2O there was added 18.62 g. PhNH_2 in Et_2O and stirred 1 hr.; after filtration there was isolated 7.5 g. $\text{PhB}(\text{OCH}_2\text{CHMe}_2)_2$, b_{21} $146-50^{\circ}$, some PhNH_2 , and 30% hexaphenylborazole, m. $380-5^{\circ}$, isolated after distn. of the above ester. Similarly $p\text{-MeC}_6\text{H}_4\text{BClOCH}_2\text{CHMe}_2$ and PhNH_2 gave $p\text{-MeC}_6\text{H}_4\text{B}(\text{OCH}_2\text{CHMe}_2)_2$, b_{10} $145-50^{\circ}$ and 39% B,B,B-tri-*p*-tolyl-N,N,N-triphenylborazole, m. $282-4^{\circ}$ (from C_6H_6 -isopentane). Heating 2.1 g. $\text{PhB}(\text{NHEt})_2$ with 0.2 ml. iso-BuOH 2 hrs. at 270° gave EtNH_2 and 85.2% B,B,B-triphenyl-N,N,N-triethylborazole, m. $205-9^{\circ}$. Treatment of 19.6 g. $\text{PhBClOCH}_2\text{CHMe}_2$ in Et_2O with 18.62 g. PhNH_2 1 hr., filtration and high vacuum distr. gave 76.9% $\text{PhB}(\text{OCH}_2\text{CHMe}_2)_2$ and 79.4% $\text{PhB}(\text{NHPh})_2$, $b_{0.06}$ $178-80^{\circ}$, m. $84-6^{\circ}$. Similarly $p\text{-MeC}_6\text{H}_4\text{BClOCH}_2\text{CHMe}_2$ gave 85.9% $p\text{-MeC}_6\text{H}_4\text{B}(\text{OCH}_2\text{CHMe}_2)_2$ and 85.6% $p\text{-MeC}_6\text{H}_4\text{B}(\text{NHPh})_2$, $b_{0.04}$ $163-5^{\circ}$, m. $100-2^{\circ}$. The latter distd. at ca. 400° gave PhNH_2 and 33.8% B,B,B-tri-*p*-tolyl-N,N,N-triphenylborazole, m. $282-4^{\circ}$.

Organoboron compounds. XXXVII. Synthesis of B-triarylborazoles from arylboron dichlorides.

B. M. Mikhailov, A. N. Blokhina and T. V. Kostroma (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 1483-6 (1959). of. prec. abstr.

The following reactions were run under N_2 . To 70 g. $PhB(OBu)_2$ there was added 62 g. PCl_5 so as to maintain the temp. at $70-80^\circ$ with water cooling and after the reaction had subsided the remaining 62 g. PCl_5 was added at once and the mixt. stirred 1 hr. on a steam bath. Distn. gave 60% $PhBCl_2$, $b_{37} 87-9^\circ$. Similarly $p-C_6H_4B(OCH_2CHMe_2)_2$ gave 50% $p-MeC_6H_4BCl_2$, $b_7 91-4^\circ$, m. $25-7^\circ$. Similarly was prepd. 66.3% $p-BrC_6H_4BCl_2$, $b_{20} 114-4.5^\circ$, m. $36-8^\circ$. Passage of NH_3 0.5 hr. into 4.3 g. $p-MeC_6H_4BCl_2$ in 50 ml. C_6H_6 , was followed by addn. of NH_3 over 1 hr. on a steam bath; the mixt. was centrifuged, evapd. and treated with isopentane yielding 64.3% B,B,B-tri-p-tolylborazole, m. $189-90^\circ$ (from C_6H_6 -isopentane). Similarly was prepd. 66.5% B,B,B-tri-p-bromophenylborazole, m. $192-3^\circ$, and 91.3% B,B,B-tri-p-chlorophenylborazole, m. $269-70^\circ$. Treatment of 2.7 g. $PhBCl_2$ in Et_2O at -10° with Et_3N gave a ppt. of $PhBCl_2 \cdot Et_3N$, m. $80-4^\circ$.

Organoboron compounds. XXXVI. Unsymmetric diarylborenic acids and their derivatives.

B. N. Mikhailov and N. S. Fedotov (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 2244-8 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1958, 419.

All reactions below were run under N_2 . Reaction of 0.4 mole $1-C_{10}H_7MgBr$ and 88.3 g. $PhB(OCH_2CHMe_2)_2$ in Et_2O at -60° gave after treatment with dil. HCl 30% $1-C_{10}H_7BPhOCH_2CHMe_2$, b_8 207-3°, d_{20} 1.099, n_D^{20} 1.597; passage of NH_3 in Et_2O soln. of this gave the NH_3 adduct, m. 90-2° (in sealed tube). Similarly was prepd. 41% $(p-MeC_6H_4)BPhOCH_2CHMe_2$, $b_{1.5}$ 126-8°, 0.9729, 1.5552; NH_3 adduct, m. 87-9°. Treatment of I with 100% excess $H_2NCH_2CH_2OH$ gave 87.3% $(p-MeC_6H_4)BPhOCH_2CH_2NH_2$, m. 163-5°. $PhB(OCH_2CHMe_2)_2$ and $p-BrC_6H_4MgBr$ gave 33% $(p-BrC_6H_4)BPhOCH_2CHMe_2$, b_2 152-3°, 1.9199, 1.5773. Treatment of 13 g. A (II) with 9.4 g. PCl_5 with heating to 50-60° gave 76.3% $1-C_{10}H_7BPhCl$, b_4 180-1°, m. 87-90°. Similarly was prepd. 50% $p-MeC_6H_4BPhCl$, b_8 142-1°, d_{20} 1.5783.

Treating I in Et_2O with N NaOH with ice cooling gave after evapn. and treatment with isopentane at -40° a low yield of $1-C_{10}H_7BPhOH$, m. 57-9°. Similarly was prepd. $p-MeC_6H_4BPhOH$, an oil, which on standing transformed into 88% $(PhBO)_3$, m. 212-4°. $p-MeC_6H_4BPhCl$ forms an equimolar adduct with dioxane, m. 72-6°. Similar adduct formed with Ph_2BCl , m. 80-5°, and with $(1-C_{10}H_7)_2BCl$, m. 93-6°, and with $1-C_{10}H_7BPhCl$, m. 90-1°. These are not stable in storage.

Organoboron compounds. XXXVII. Lithium salts of diarylboronic acids and their complex compounds with dioxane.

B. M. Mikhailov and V. A. Vaver (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 29, 2248-53 (1959). cf. preced. abstr.

Diarylboronic acids react like protonic acids in nonaqueous media. All the reactions below were run under N_2 . Addn. of 0.018 mole BuLi soln. to 5 g. $(1-C_{10}H_7)_2BOH$ in dry C_6H_6 gave in 10 hrs. a crystn. ppt. of its Li salt. Similarly $(p-MeC_6H_4)_2BOH$ and $p-MeC_6H_4Li$ gave the Li of the former acid, a crystn. solid. ~~Reacting with BuLi in hexane- C_6H_6 gave a ppt. of mixed $(o-MeC_6H_4)_2BBuOH.Li$ and its cleavage products $(o-MeC_6H_4)_2BLi$ and $(o-MeC_6H_4)BBuOLi$. This mixt. treated with dioxane in Et_2O gave on evapn. of the org. layer and treatment with isopentane in the cold a ppt. of $(o-MeC_6H_4)_2BOLi.O(CH_2CH_2)_2O$, which also formed from $(o-MeC_6H_4)_2BOH$ and $o-MeC_6H_4Li.O(CH_2CH_2)_2O$. The latter procedure also gave from $p-MeC_6H_4Li.O(CH_2CH_2)_2O$ and $(p-MeC_6H_4)_2BOH$ in Et_2O -dioxane a ppt. of relatively insol. $(p-MeC_6H_4)_2BOLi.O(CH_2CH_2)_2O$, while the filtrate gave $(p-MeC_6H_4)_3BOH.Li.O(CH_2CH_2)_2O$. $(1-C_{10}H_7)_2BOH$ in Et_2O forms a dioxane adduct, m. $130-1^\circ$, which with BuLi gave $(1-C_{10}H_7)_2BOLi.O(CH_2CH_2)_2O$. Treatment of $(1-C_{10}H_7)_2BOLi$ with Me_2SO_4 in C_6H_6 gave 72.3% $(1-C_{10}H_7)_2BOMe$, m. $101-3^\circ$. $(1-C_{10}H_7)_2BOLi$ and $MeOH$ in Et_2O gave in 15 min. $(1-C_{10}H_7)_2B(OMe)OH.Li.Et_2O$.~~

Magnetic susceptibility of some oxalate complexes of tetravalent uranium.
T. G. Aminov, V. V. Zelentsov and I. A. Savich (Phys.Tech.Inst., Moscow).
Doklady Akad. Nauk S.S.S.R. 128, 533-5(1959).

The following av. values of effective magnetic moment and Weiss constants were detd. conventionally: $K_4[U(C_2O_4)_4] \cdot 5H_2O$ 3.62 and 60; $Ba_2[U(C_2O_4)_4] \cdot 6H_2O$ 3.60 and 132; $Cd_2[U(C_2O_4)_4] \cdot 7H_2O$ 3.85 and 117. Variation of susceptibility with temp. is shown by suitable curves and all the above salts are found to obey the Curie-Weiss law above 195°K. At lower temp. the deviations are caused by formation of low temperature magnetic anomalies and the susceptibility rises more slowly with declining temp. than expected. The effective moments, above, indicate the state of 3H_4 for U, with the 2 unpaired electrons being in the 5f level.

1/1 arm

Some rules of polymerization of propylene with the catalytic system of $TiCl_4 + AlR_3$.

A. V. Topchiev, B. A. Krantsel and L. G. Sidorova. Doklady Akad. Nauk S.S. S.R. 128, 732-5 (1959).

Polymerization of C_3H_6 with $TiCl_4 - (iso-Bu)_3Al$ was examined in detail. The chain polymerization process yields within 17 sec. of initiation a polymer with high mol. wt. which remains nearly unchanged over the continued polymerization period of 1.5 hrs. Since the catalyst gradually loses its effectiveness, the rate of reaction declines with time (shown graphically), but if R_3Al is gradually added to the system over several hrs. the activity of the system remains at high level and the polymer yield is raised. Addn. of O_2 raises the yield to a max. at about 0.026 vol.% O_2 , after which further addn. of O_2 has a negative effect on the yield. Characteristic viscosity of the polymer declines steadily with elevation of temp. of polymerization (25-80°). It is suggested that the solid phase of the catalyst present in the reaction zone aids the stereospecificity of the polymerization.

Organozinc compounds of Ar_2Zn class and their dioxanates.

A. I. Steverdin, L. V. Shramova and E. A. Kocheshkov (L. Ya. Karpov Phys. Chem. Inst., Moscow). Doklady Akad. Nauk S.S.S.R. 125, 320-2 (1959). cf. 124, 602 (1959).

All expts. described below were run under inert atm. To a well stirred mixt. of 18.8 g. solid $PhLi$ and 14.8 g. dry $ZnCl_2$ powdered under A, there was added 150 ml. xylene, followed by 30 ml. Et_2O (exothermic) and the mixt. heated 5-5.5 hrs. at reflux; the soln. was filtered at $70-80^\circ$ from Li halide ppt. and the filtrate evapd. in part to yield 83.3 colorless crystalline Ph_2Zn , m. 105° . Treated with dioxane this gave $Ph_2Zn \cdot C_4H_8O_2$, crystalline solid, sol. in dioxane and Et_2O ; it is decompd. by H_2O or $EtOH$. Similarly there was prepd. 71% $(o-MeC_6H_4)_2Zn$, m. $69-71^\circ$; 45% $(p-MeC_6H_4)_2Zn$, m. $169-70^\circ$ (dioxanate, a colorless crystalline solid); $(1-C_{10}H_7)_2Zn$, 49.5%, dec. 200° (dioxanate, colorless solid).

Germanium

Addition of trichlorogermanium to acetylene, olefins and their derivatives in the absence of catalysts.

A. D. Petrov, V. F. Pironov and N. C. Dzhurinskaya (N.D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R., 128, 302-4 (1959).

cf. Kochlov et al. J. Org. Chem. 19, 5873 (1954)

Passage of a rapid stream of HCl through 50 g. particulated Ge and 10 g. pptd. Cu at 450° gave 79% HGeCl_2 , b. 77-8°. This (18 g.) added to 5.3 g. $\text{CH}_2=\text{CHCN}$ at 60-70° (exothermic) gave 53% $\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{CN}$, b_{22} 135°, n. 37.7°. Similarly $\text{CH}_2=\text{CHCH}_2\text{Cl}$ gave 77.4% $\text{Cl}_3\text{Ge}(\text{CH}_2)_3\text{Cl}$, b_{20} 105°, n_D^{20} 1.5070, d_{20} 1.6636. $\text{CH}_2=\text{CHCH}_2\text{Cl}$ gave 53.3% $\text{Cl}_3\text{GeCH}_2\text{CHMeCH}_2\text{Cl}$, b_{11} 90-3°, 1.5000, 1.5758. $\text{CH}_2=\text{CHSiCl}_3$ gave 33% $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{GeCl}_3$, b_{15} 120°, n. 35°. Passage of C_2H_2 into HGeCl_3 until the exothermic reaction ceased, gave 90% $\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{GeCl}_3$, b_{12} 130-1°, n. 56°. Similar reaction with C_2H_4 gave 55% EtGeCl_3 , b_{761} 141.5° 1.4745, 1.6091. 1-Octene gave 55% $n\text{-C}_8\text{H}_{17}\text{GeCl}_3$, b_{15} 130°, 1.4720, 1.2712. $\text{CH}_2=\text{CHCH}_2\text{OAc}$ gave 40.8% $\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{CH}_2\text{OAc}$, b_{12} 127-80, 1.4855, 2.5392. $\text{CH}_2=\text{CHCl}$ gave 52.5% $\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{Cl}$, b_{15} 75°, 1.5092, 1.7637. $\text{Cl}_3\text{SiCH}=\text{CHCl}$ gave 52% $\text{Cl}_3\text{GeCHClCH}_2\text{SiCl}_3$, b_{13} 129°, 1.5268, 1.8350. In none of the above addn. reactions was it necessary to add any catalysts or to heat the mixts. in autoclaves. Evidently HGeCl_3 has more pronounced additive properties in respect to unsatd. bonds than displayed by HSiCl_3 .

arsenic

Thermal decomposition of organic compounds of pentavalent arsenic.

G. Kanaai and B. D. Chernokal'skii (S.M.Kirov Chem. Technol. Inst., Kazan).
Doklady Akad. Nauk S.S.S.R. 123, 299-301 (1959).

cf. Iann et al. J.Chem.Soc. 1949,71.

Pyrolyses of the following substances were performed in *distn.* app. at 200-200°. PrAs(O)(OEt)_2 (b_{11} 121.5-4°, d_{20} 1.2435, n_D^{20} 1.4520) was 40.7% unchanged and gave 11.2% PrOAs(OEt)_2 , b_{10} 56-9°, 1.1623, 1.4413. PrAs(O)(OPr)_2 similarly gave 3.4% PrOH . PrAs(O)(OBu)_2 gave 17.1% BuOH , 5.7% PrAs(OBu)_2 , b_{12} 111-15°, 1.0573, 1.4523 and 2.1% $\text{C}_{11}\text{H}_{25}\text{O}_3\text{As}$, b_{11} 121-5°, -, 1.4496. MeAs(O)(OBu)_2 gave 9.3% BuOH and 12.5% MeAs(OBu)_2 , b_{13} 93-5°, 1.0846, 1.45-15. EtAs(O)(OBu)_2 gave 15.5% BuOH and 19.6% EtAs(OBu)_2 , b_{13} 103-6°, 1.0727, 1.4534. The latter reaction also gave an unidentified carbonyl compound.

Oxidation of R_2AsOR with SeO_2 gave $\text{R}_2\text{As(O)OR}$. Thus were prepd.: from Et_2AsOEt - 1.5% $\text{Et}_2\text{AsO}_2\text{H}$, m. 136-7°, and 2.1% Et_2AsOEt , b. 140-1°, d_{20} 1.1148, n_D^{20} 1.4600; from Et_2AsOPr - 16.6% PrOH , 2.7% $\text{Et}_2\text{AsO}_2\text{H}$, m. 135-7°, and 6.3% Et_2AsOPr , b_{13} 54.5-7°, 1.0904, 1.4621; from Et_2AsOBu - 12.1% $\text{Et}_2\text{As(O)OBu}$, b_4 130-30.5°, 1.1922, 1.4721, 11.9% $\text{Et}_2\text{AsO}_2\text{H}$ and 2% EtAs(OBu)_2 , b_{11} 93.5-101°, -, 1.4522; from MeBuAsOEt - 26% MeBuAs(O)OEt , b_2 110-11°, 1.3365, 1.4739 and 11.1% $\text{MeBuAsO}_2\text{H}$, m. 116-8°; from MeBuAsOBu - 1.9% BuOH , 24.9% MeBuAs(O)OBu , b_3 133-4°, 1.1507, 1.4673, and 5.5% $\text{MeBuAsO}_2\text{H}$, m. 126-7°. Thus the conversion of $\text{R}_2\text{AsO}_2\text{R}$ to R_2AsOR is very facile. The latter esters are readily hydrolyzed with H_2O and atm. moisture. Atomic refraction of As in these compds. is estd. at 8.19. Pyrolysis of R_2AsO gave: from Et_2AsO 2.9% EtOH , 54.4% Et_3As ; from Pr_2AsO 5.9% PrOH and 35.8% Pr_3As ; from Me_2BuAsO 23.7% Me_2BuAs , b. 133-5°, 1.0560, 1.4673 and 1.9% MeBuAs(OBu) , b_{11} 33-5°, -, 1.4611; from MeBu_2AsO 3.9% PrCHO , 8% BuOH , 14.9% MeBu_2As , b. 76-6.5°, 1.0103, 1.4724, 2.5% Bu_3As , b_{10} 114-6°, 0.9886, 1.4716, and 0.8% $\text{Bu}_2\text{As(OMe)}$, b_{13} 86-7.5°, -, 1.4685.

Determination of organoaluminum compounds by the indicator method.

G. A. Rasuvayev and A. I. Graevskii. Doklady Akad. Nauk S.S.S.R. 128, 309-11 (1959).

AlR_3 and their halogen deriva. may be detd. by adding their soln. in O-free $MePh$ to soln. of Methyl violet in $(CH_2Cl)_2$. The color changes from violet to yellow or green; addn. of an org. base reverts the color back to violet. Compounds of types R_2AlOR or $Al(OR)_2$ do not produce this color change, possible owing to screening of their 3p level electrons by the unshared O electron pairs. Titration of R_3Al and their halogen analogs with org. bases such as $BuOAc$, $EtOAc$, Me_2NPh , Et_2O , pyridine results in a clean endpoint when indicators such as Methyl violet, Crystal violet or Gentian violet are used. The titration curves resemble those of strong-acid strong-base titration curves. Me_2NPh reacts with such Al compds. in 1:1 ratio. Et_2AlBr and $EtAlCl_2$ differ in acid strength from Ph_3Al and Ph_2AlBr . Et_2AlBr behaves like a dibasic acid. It is possible to titrate Et_2AlCl and $EtAlCl_2$ separately in a mixt. On the basis of detn. of acid strengths by Hantzsch's method (Ber. 62, 975 (1929)) the following ascending series of acid strengths was established: Et_3Al , Et_2AlCl , Et_2AlBr , $EtAlCl_2$. The solns. for the titrations must be dil. as solns. with 30-40% R_3Al destroy the indicators. $MePh$, xylene, petroleum fraction and heptane may be used as solvents.

Synthesis of polyorganostannoxanes.

M. M. Koton and T. M. Kiseleva (High Polymer Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 130, 86-7 (1960).

Heating a 1:1 molar mixt. of $(\text{EtO})_4\text{Sn}$ with $\text{iso-Bu}_2\text{Sn}(\text{OAc})_2$ (b₁₀ 140-1°) 28 hrs. at 140° in inert atm. gave 74.6% EtOAc and a residue of yellowish insol. solid, does not m. 250°, contg. 58% Sn; extrn. with C_6H_6 gave a yellowish polymer $\text{C}_{52}\text{H}_{120}\text{O}_{15}\text{Sn}_8$, m. 70-5°, which is hydrolyzed by H_2O to a colorless insol. and infusible solid $\text{C}_{32}\text{H}_{74}\text{O}_{10}\text{Sn}_8$. Apparently the sol. polymer was $\text{HO}(\text{SnR}_2\text{OSnO})_n\text{OH}$. Similarly $(\text{EtO})_4\text{Sn}$ and $\text{Bu}_2\text{Sn}(\text{OAc})_2$ (b₁₀ 146-7°) gave an insol. solid contg. 57% Sn and a sol. polymer, m. 60-70°, whose mol. wt. was about 2000.

tin